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Jack Ohr, et al

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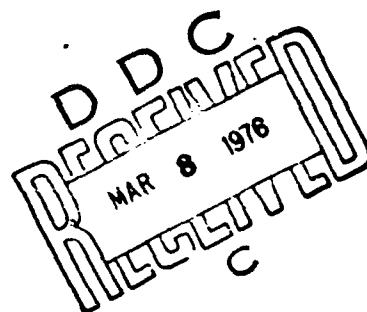


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Work Unit No. GC312



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The hexavalent anionic partner to the dibenzo-18-crown-6 and 18-crown-6 complexes made according to U. S. Patent Application Serial No. 511328 (Allowed) by Ohr and Clark was determined to be Chlorochromate, CrO₃Cl⁻. The complexes when dissolved in small amounts in paint coatings provide good corrosion protection to aircraft metals such as aluminum, steel, and magnesium; but are impractical for Fleet use at this time because of their poor storage stability properties.		

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INTRODUCTION

The Part I report demonstrated that it was possible to impart a high degree of corrosion inhibition to organic solvent-based aircraft topcoats without seriously affecting their color by dissolving (not dispersing) therein small amounts of complexed hexavalent chromium salts (references (a) to (f)) prepared according to the authors' patented method (reference (g)). The report covered by this investigation explores the chemical nature of the complexes; i.e., the anionic species containing the hexavalent chromium, and the practicality of using the complexes as paint additives at this time to solve Fleet corrosion problems. We choose to designate the hexavalent chromium complexes as "AMEchromes", regardless of macrocycle source.

The work reported herein was conducted under AIRTASK NO. ZF 61412001, IED Work Unit No. GC 312.

EXPERIMENTAL PROCEDURES

Preparation and Purification of 18-Crown-6 (reference (h))

A three-liter, three-neck flask equipped with mechanical stirrer, reflux condenser, and addition funnel is charged with triethylene glycol (112.5 g, 0.75 mole) and tetrahydrofuran (600 ml). Stirring is commenced and 60% KOH solution (109 g of 85% KOH in 70 ml water) is poured in. The solution warms but does not boil. After about 15 min of stirring (when the solution darkens) a solution of 3,6-dioxo-1, 8-dichlorooctane (140.3 g, 0.75 mole) in THF (100 ml) is added in a stream. After the addition is complete, the solution is heated at reflux and stirred vigorously for 18 hours. The solution is allowed to cool and the bulk of the THF is evaporated under reduced pressure. The resulting thick brown slurry is diluted with 500 ml dichloromethane and filtered. The salts removed by filtration are washed with more dichloromethane to remove adsorbed crown, and the combined organic solution is dried over $MgSO_4$, evaporated to minimum volume (aspirator vacuum), and then distilled at high vacuum. The distillation should be carried out at the lowest possible pressure; a typical fraction contains 80 g and is collected over 100-160°C at 0.2 mm Hg.

To 50 g of crude 18-crown-6 (bp 125-160°C, 0.2 mm) in a 250 ml Erlenmeyer flask is added 125 ml acetonitrile. The resulting slurry is heated on a hot plate to effect solution. A magnetic stirring bar is added and the neck equipped with a $CaSO_4$ drying tube. The solution is stirred vigorously as it is allowed to cool to ambient temperature, and fine white crystals of crown-acetonitrile complex are deposited. The flask is finally cooled in an ice-acetone bath to precipitate as much complex as possible, and the solid then collected by rapid filtration. The hygroscopic crystals are transferred to a 500 ml round-bottom flask equipped with a magnetic stirring bar and vacuum take-off. The acetonitrile is removed from the complex at high vacuum (0.1 - 0.5 mm) with gentle heating ($t \leq 40^\circ C$) over two to three hours. The pure, colorless crown (20 - 30 g, 40 - 60%) crystallizes on standing and

shows no ions above $m/e = 265$ in the mass spectrum and no significant hydroxyl vibration in the 3500 cm^{-1} region of the infrared. The pure crown has mp $36.5 - 38.0^\circ\text{C}$ (lit. mp $39 - 40^\circ\text{C}$) (reference (1)); nmr (60 MHz, CCl_4): 3.56 ppm (singlet); ir (neat): 2875 (alkane CH), 1450 and 1350 (alkane CH), and 1120 cm^{-1} (ether link); mass spectrum: M and M+1 at 264 and 265, other fragments at $m/3 = 89, 87, 59, 45, 44, 43$, and 31. See Figures 1 and 2 for IR and NMR of compound.

Preparation of the Potassium Chlorochromate of 18-Crown-6 (reference (g))

A 0.7M solution of 18-crown-6 was prepared in methylene chloride and 200 ml of it was placed in a 500 ml separatory funnel. Next, 500 ml of an acidified aqueous solution of hexavalent chromate was prepared as follows: 50 gm K_2CrO_4 , 500 ml water and 96 gm of 37% constant boiling HCl. A 200 ml portion of this solution was added to the same separatory funnel. The funnel was vigorously shaken and the organic phase removed, dried over MgSO_4 , filtered, evaporated to about 125 ml and crystallized at -5°C . The product is orange crystals which decomposes over a long range of temperature beginning at approximately 150°C .

Elemental Analysis:

	<u>Theory</u>	<u>Found</u>
LC	32.84	32.92
LE	5.51	5.62
LC1	8.08	7.66

Further proof that the complex is as designated is indicated by the data of Table I which shows that the maximum molar extinction coefficient values for the complex and for the potassium chlorochromate salt per se are reasonably close for the same wave lengths. See Figures 3 and 4 for IR and UV spectra of complex.

Preparation of Potassium Chlorochromate (Prepared according to Mellor) (reference (j))

A 6 Molar HCl solution was prepared by diluting 85 grams of 36% HCl to 150 ml with water. To this was added 25 grams of potassium dichromate while heating and stirring. The solution was allowed to crystallize undisturbed for three days at room temperature and then suction filtered. The orange crystals were dried under vacuum. See Figures 5 and 6 for UV and IR spectra of compound.

Preparation of Potassium Chlorochromate of Dibenzo-18-Crown-6

The preparation was very similar to the potassium chlorochromate of 18-crown-6 above. The crystals were orange-yellow.

	<u>Theory</u>	<u>Found</u>
LC	44.90	44.53
LE	4.52	4.39
LC1	6.64	7.00

See Figure 7 for UV of complex.

TABLE I

COMPARISON OF UV ABSORPTION DATA FOR THE POTASSIUM
CHLOROCHROMATE COMPLEX OF 18-CROWN-6 vs POTASSIUM CHLOROCHROMATE PER SE

COMPLEX (1)

λ_{MAX}	A	$\epsilon_{\text{MAX}} \text{ (l/g-cm)}$	$\epsilon_{\text{MAX}} \text{ (l/mol-cm)}$ (2)
363	0.64	2.71	1190
354	0.64	2.69	1180
283	0.91	3.86	1695
244	1.07	4.53	1990

SALT

λ_{MAX}	$\epsilon_{\text{MAX}} \text{ (l/mol-cm)}$
363	1180
353	1160
282	1650
240	1780

NOTES:

(1) Complex values are from Figure 4

(2) A molecular weight of 439 was assumed based on the complex, (18-Crown-6) (KCrO_3Cl). Since a concentration of 0.236 gm/liter was prepared, this corresponds to a 5.37×10^{-4} Molar solution. These values were used for c in the Beer-Lambert expression $A = \epsilon bc$

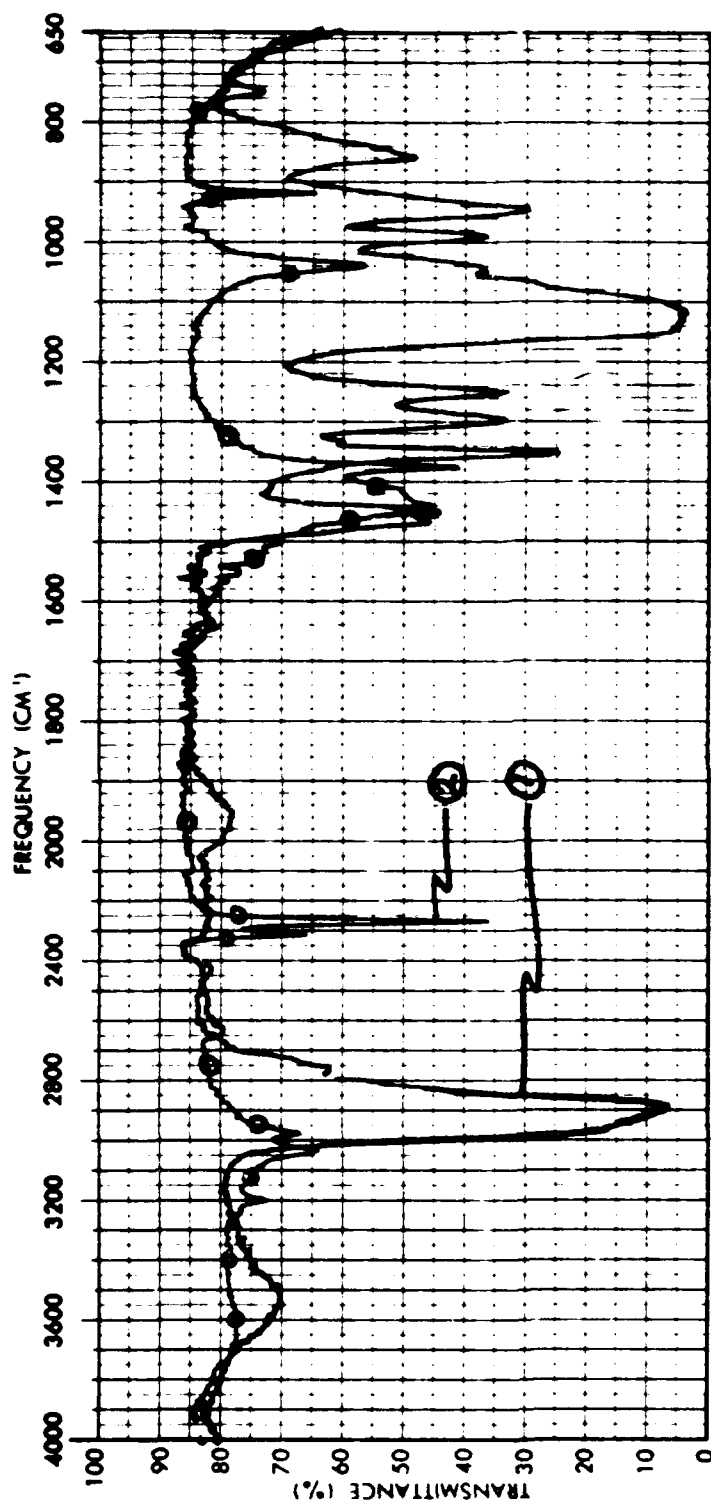


FIGURE 1 — IR of 18—CROWN—6 vs THE PURIFICATION SOLVENT, ACETONITRILE.

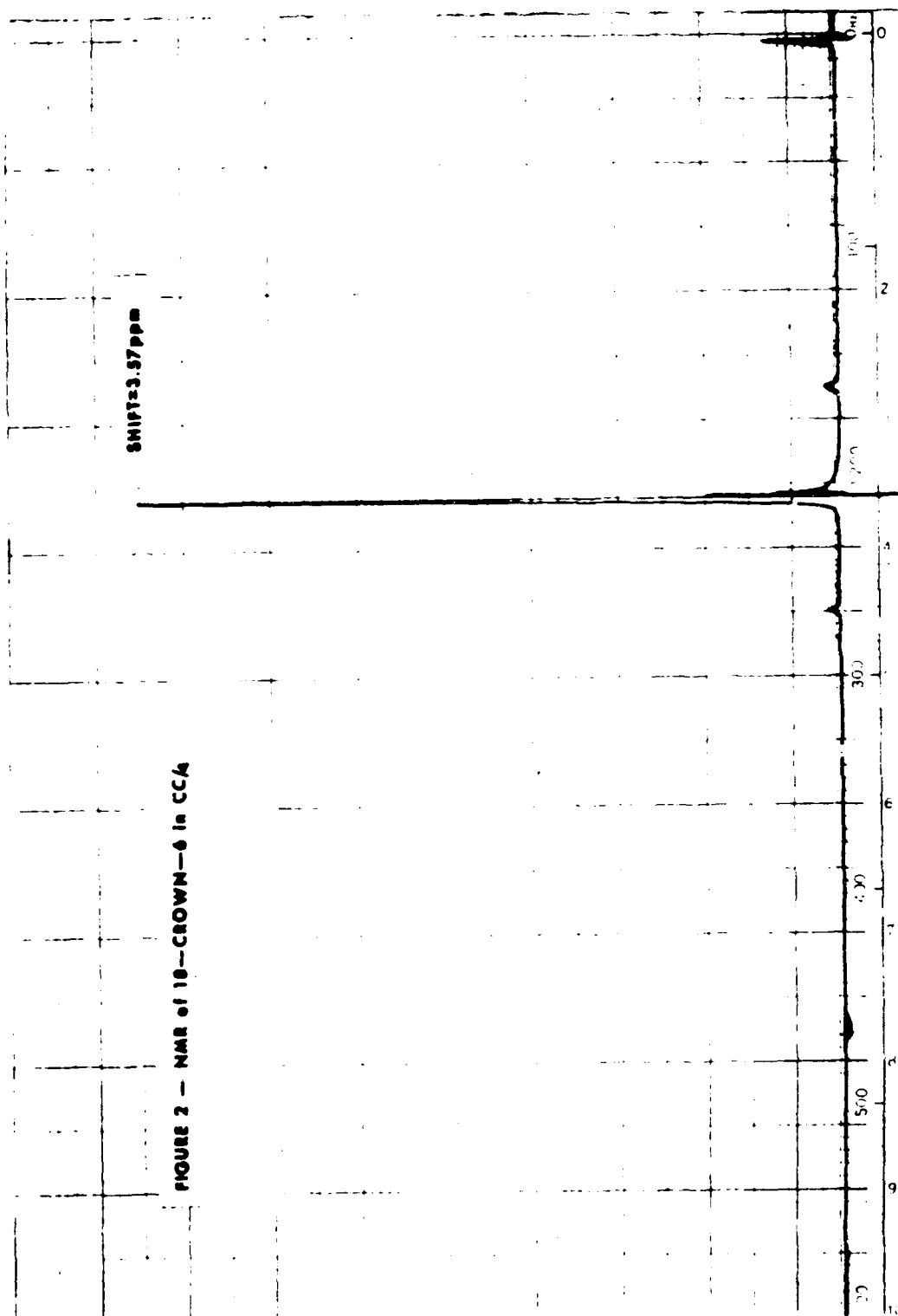


FIGURE 2 - NMR of 18-CROWN-6 in CCl₄

Figure 2. NMR of 18-CROWN-6 in CCl₄

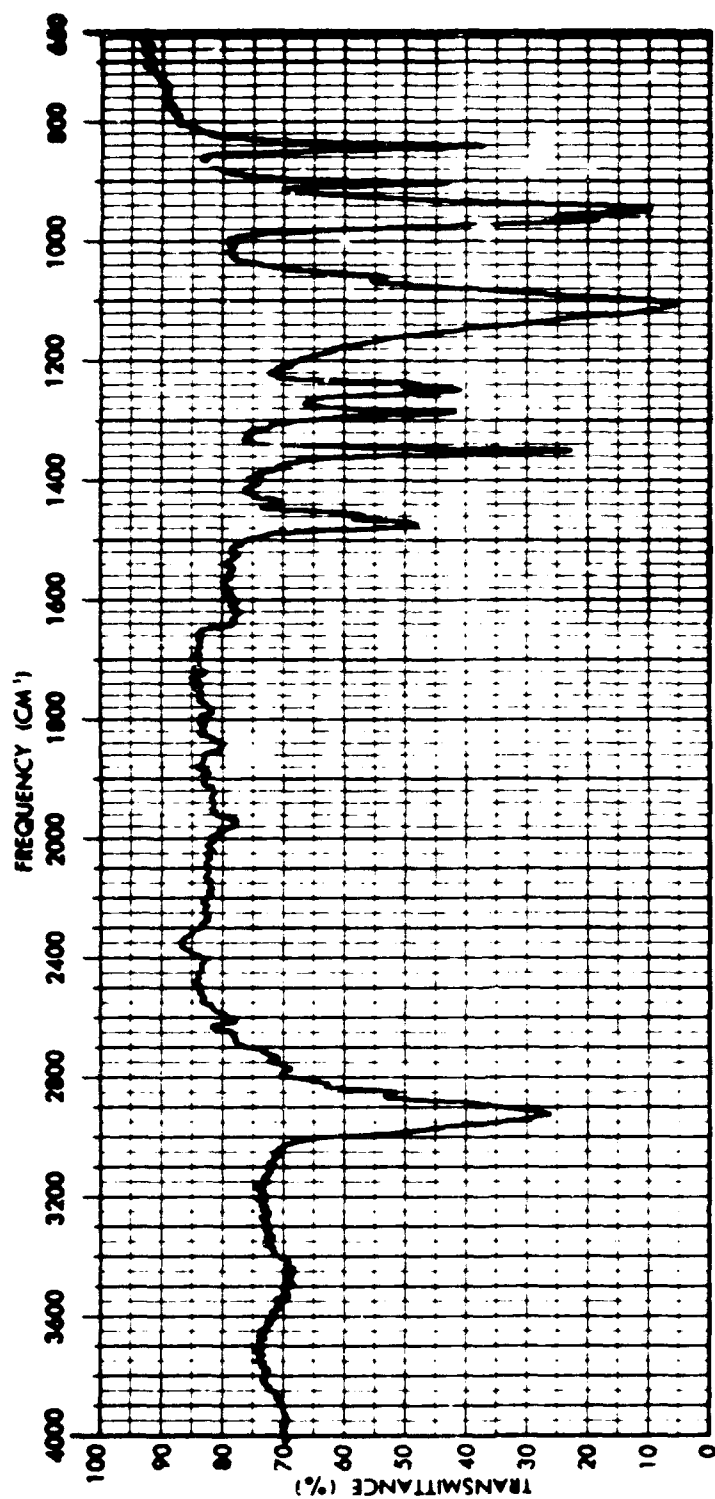


FIGURE 3 — IR of POTASSIUM CHLOROCHROMATE COMPLEX of 18-CROWN-6.

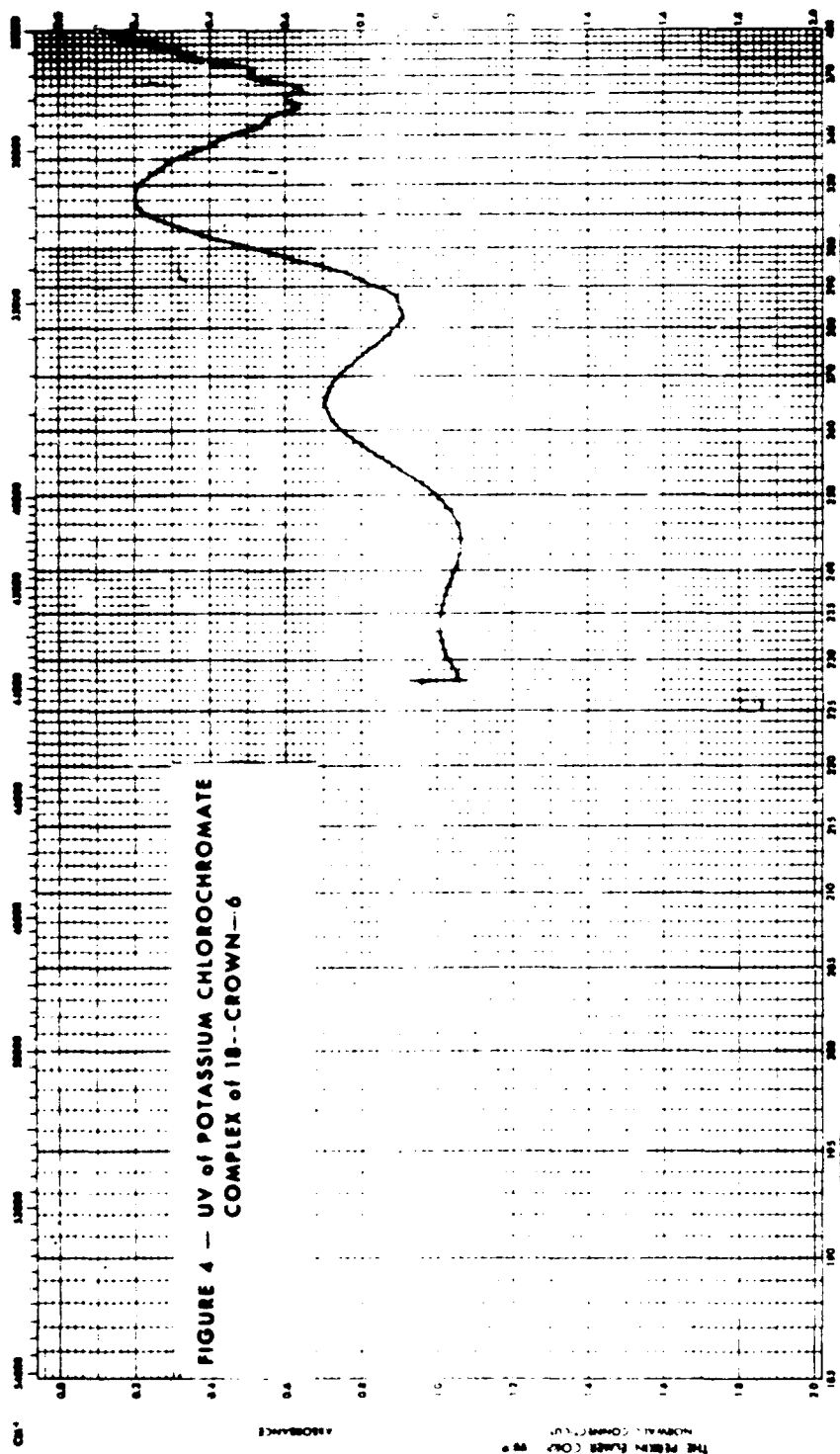


Figure 4. UV of Potassium Chlorochromate Complex of 18-CROWN-6

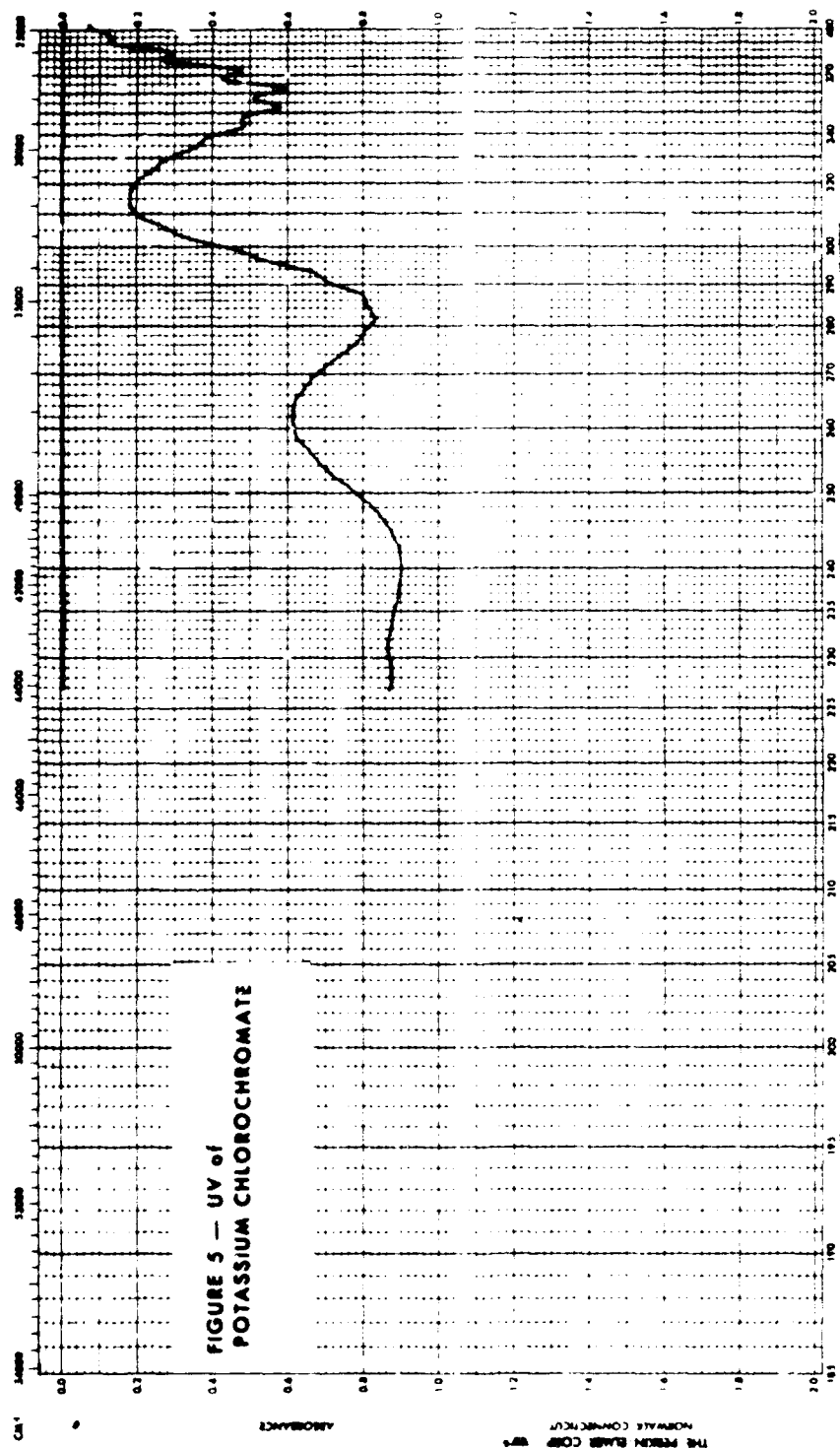


Figure 5. UV of Potassium Chlorochromate

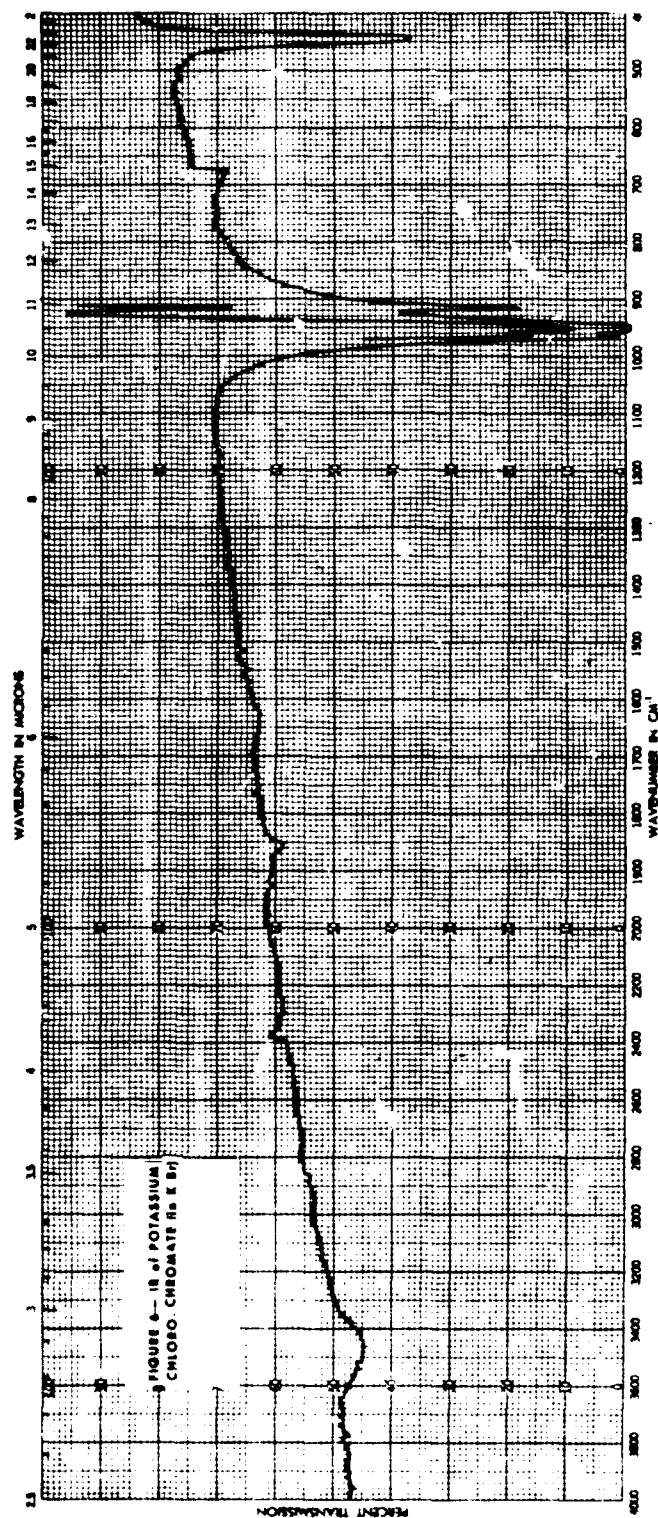


Figure 6. IR of Potassium Chlorochromate (in K Br)

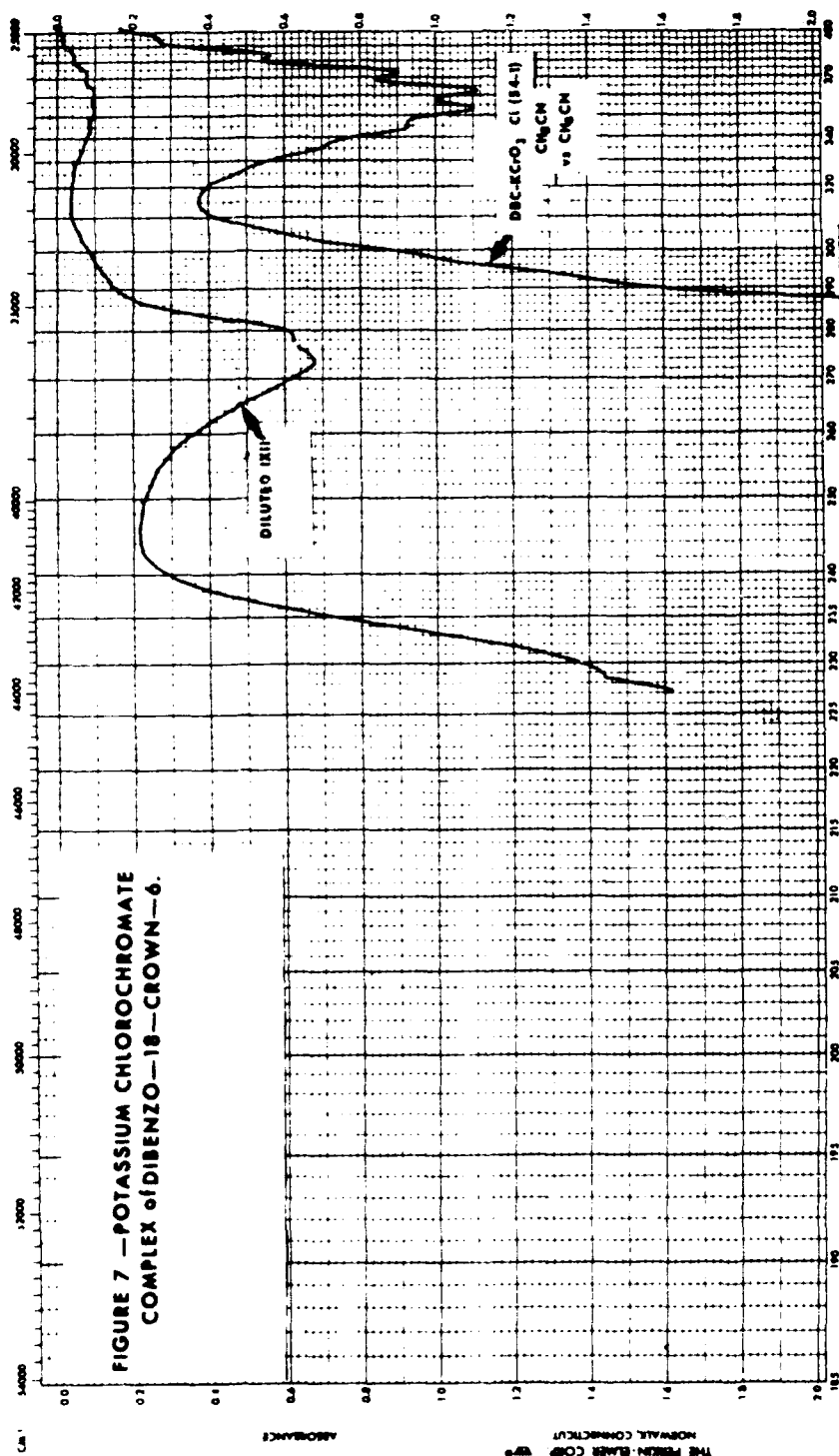


Figure 7. Potassium Chlorochromate Complex of Dibenzo-18 CROWN-6

RESULTS

1. The 18-crown-6 and dibenzo-18-crown-6 complex systems when prepared according to reference (g) produced chlorochromate, CrO_3Cl^- (reference (k)) as anionic partner to the complexed potassium cation as illustrated in Figure 1. Such hexavalent chromium systems we choose to designate as AMChromes.
2. The 18-crown-6 was synthesized according to reference (h) in an overall yield of 18%.
3. The 18-crown-6 AMChromes exhibited rapid deterioration at room temperature, even under nitrogen, so that after a few weeks the clear AMChromes had changed to a deep brown viscous mass. Presumably, the product is a polymer resembling a polyether since no significant changes appeared in the infrared for the before and after situations. The product is completely insoluble in methylene chloride, the best solvent for the AMChromes. Moreover, gases are produced during the oxidation which could be a fire hazard if stored in large enough quantity.

CONCLUSIONS

1. The AMChromes when prepared according to reference (g) consist of a complexed potassium cation with chlorochromate, CrO_3Cl^- , as the anionic partner.
2. Even though the AMChromes are effective corrosion inhibiting agents for paint coatings, they have poor shelf lives and hence are impractical (and even hazardous) for Fleet use at this time.

RECOMMENDATIONS

1. It is recommended that this research be terminated on the basis that further work for increasing the shelf life of the AMChromes does not appear promising. Accordingly, this is considered to be a final report on the AMChromes research.

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